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91 6 4 087

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION NONE			1b. RESTRICTIVE MARKINGS NONE		
2a. SECURITY CLASSIFICATION AUTHORITY NONE			3. DISTRIBUTION / AVAILABILITY OF REPORT UNLIMITED		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE NONE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 8			5. MONITORING ORGANIZATION REPORT NUMBER(S) ONR N0014-89-J-1028		
6a. NAME OF PERFORMING ORGANIZATION University of Southern Mississippi		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Polymer Science Department Southern Station Box 10076 Hattiesburg, MS 39406-0076			7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Avenue Arlington, VA 22217			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
11. TITLE (Include Security Classification) Photodegradation of Polyimides III. The Effect of Chemical Composition, Radiation Source, Atmosphere, and Processing					
12. PERSONAL AUTHOR(S) C.E. Hoyle and E.T. Anzures					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 6-1-90 TO 5-31-91		14. DATE OF REPORT (Year, Month, Day) 91-05-31	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION		
22a. NAME OF RESPONSIBLE INDIVIDUAL Ken Wynne			22b. TELEPHONE (Include Area Code) (601) 266-4868		22c. OFFICE SYMBOL

Photodegradation of Polyimides.III.
The Effect of Chemical Composition, Radiation Source,
Atmosphere, and Processing

by

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ABSTRACT

Polyimide films made from diarylanhydrides with oxygen, carbonyl, and hexafluoroisopropylidene 6F bridging groups are photolabile when irradiated with unfiltered light from a medium pressure mercury lamp. The presence of oxygen is necessary to the photolytic degradation process, which results in the ultimate oxidative ablation of thin polyimide films. Films based on the 6F dianhydride containing a hexafluoroisopropylidene hinge group are the most unstable. However, photolysis of 6F dianhydride based polyimides in an inert atmosphere with either the unfiltered medium pressure mercury lamp or an electron beam results in no detectable changes even after long exposure times.

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INTRODUCTION

We have previously reported (1-3) the photolytic decomposition of aromatic polyimide films based upon oxydianiline (ODA) and a dianhydride comprised of two phenyl rings with a hexafluoropropylidene bridging group, i.e., the 6F dianhydride. The 6F-ODA films when exposed to the unfiltered output of a medium pressure mercury lamp in air were found to rapidly decompose at a much greater rate than similar polyimide films based upon pyromellitic dianhydride (PMDA) and oxydianiline (ODA). Since aromatic polyimides have potential use in a variety of environments and can be made with considerable latitude with respect to structure and processing conditions, it is of interest to consider the effects of variation of chemical structure and physical parameters on the photodecomposition process. This paper describes results obtained in our laboratory dealing with (a.) the consequences of the chemical structure of the dianhydride and diarylamine on the photodecomposition process, (b.) the effect of processing conditions on the polyimides generated and the resultant impact, if any, on the photochemistry, and (c.) variation of the atmosphere and source of irradiation.

The effect of structure will be considered first. Based on these results, atmospheric and processing effects will be enumerated.

EXPERIMENTAL

Materials. Pyromellitic dianhydride ((PMDA, Aldrich) was crystallized from methyl ethyl ketone and vacuum sublimed prior to use. The 3,3',4,4'-benzophenone

tetracarboxylic dianhydride (BTDA, Aldrich) was washed with dry methyl ethyl ketone and vacuum sublimed before using. 4,4'-Oxydiphthalic anhydride (ODPA, Occidental Chemical) was washed with dry MEK and vacuum sublimed. Polymer grade hexafluoroisopropylidene-2,2'-bis(phthalic anhydride) (6FDA, Hoechst Celanese) was used without further purification for the lower molecular weight polyamic acid synthesis. The electronic grade 6F was vacuum sublimed prior to use for the higher molecular weight polyamic acid synthesis. 4,4'-Oxydianiline (ODA, American Tokyo Kasei) was recrystallized from ethanol and sublimed under vacuum. 4,4'-Methylenedianiline (MDA, Aldrich) was vacuum distilled.

Dimethylacetamide (DMAc, Aldrich) used for the polymerizations and the viscometric analyses was dried over molecular sieves and fractionally distilled under vacuum from calcium hydride. Tetrahydrofuran (THF, J.T. Baker A) used in the GPC analysis was distilled under nitrogen from calcium hydride.

Synthesis. The preparation of the polyimide thin films of lower molecular weight has been described in the first two papers in this series (1,2). The polyimides which were cured at different maximum temperatures were synthesized by using a procedure similar to the previous method (1,2) except DMAc was freshly distilled in an effort to produce higher molecular weight polyamic acids. The as cast films were placed in a vacuum oven at room temperature for 30 minutes to produce tacky films. Thermal curing was carried out in a Blue M Inert Gas Oven. Purging took place for 30 minutes at an elevated nitrogen flow rate (75 SCFH) to remove the air from the sample chamber. The temperature program involved 1 hour at 100 °C, 1 hour at 200 °C, and 1 hour at a

maximum cure temperature. The maximum cure temperatures used were either 250, 300, 350, 400, or 450 °C. Heating and cooling occurred at approximately 5 °C per minute and 2 °C per minute respectively. A continuous nitrogen purge (22.5 SCFH) was maintained throughout the thermal curing process. Under these conditions a positive pressure of nitrogen was maintained in the sample chamber throughout the curing process.

After curing, the films and glass plates were placed in hot water to facilitate the removal of the polyimide films. FT-IR analyses of the films showed them to be essentially fully imidized. The characteristic imide bands at 1780 (imide I), 1720 (imide I), 1370 (imide II), and 720 (imide IV) cm^{-1} were seen in the FT-IR spectra of all the cured films. The thickness of the thermally cured films (free-standing) formed from 4 mil wet polyamic acid (15 wt.% solids in DMAc) was determined using a digital micrometer. Ten pieces of polyimide film cured at 300 °C were layered on top of one another and found to have a total thickness of 0.050 mm or an average thickness of $\sim 5 \mu\text{m}$ (0.2 mil). All the polyimide films possessed similar thicknesses.

Chemical imidization of soluble polyimides was carried out in solution. The polyamic acid intermediates were synthesized according to the route described previously. For each amic acid to be cyclized, three moles each of pyridine (basic catalyst) and acetic anhydride (dehydrating agent) were added. After stirring for 13 hours under nitrogen at room temperature, the resulting polyimide was precipitated in water. The product was washed extensively with distilled water and dried under vacuum at 120 °C.

Instrumentation. Infrared absorption spectra were obtained using a Perkin-Elmer 1600 Fourier transform infrared (FT-IR) spectrophotometer with 16 spectral scans averaged at 4 cm^{-1} resolution. A Perkin-Elmer Lambda 6 UV-VIS spectrophotometer with 1 nm resolution was used to record the UV absorption spectra. The fluorescence spectra were obtained from a SPEX Fluorolog-2 spectrofluorometer using 1.5 mm slit widths for the excitation and emission monochromators. The fluorescence from films was measured in the front face geometry. Fluorescence spectra were divided by the emission from a standardized rhodamine B solution to account for fluctuations in lamp intensity with time. All spectra were corrected. Correction files in the Spex software were used to compensate for wavelength-dependant factors (e.g. detector response, monochromator transmission, etc.).

Thermal Analysis. A DuPont 9900 thermal analyzer was used for the thermogravimetric analysis (TGA) and DSC scans. DSC and dynamic TGA scans were obtained with $10^{\circ}\text{C}/\text{min}$. temperature ramps. During the TGA experiments a continuous flow of the desired gas (nitrogen or air) was maintained through the sample compartment. The reported glass transition temperatures were taken as the maximum in the first derivative.

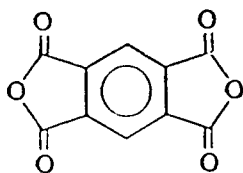
Film Photolysis. The film photolyses were conducted using a 450 W Canrad Hanovia medium pressure mercury lamp in air. The lamp output was either unfiltered or filtered through Pyrex. In the case of photolyses conducted under nitrogen, polymer films were placed in an aluminum sample chamber fitted with a quartz window. Initially the sample chamber was flushed with nitrogen for one hour at $100\text{ mL}/\text{min}$. A continuous

nitrogen flow of 100 mL/min. was maintained throughout the photolysis. The films were placed approximately 9 cm from the lamp.

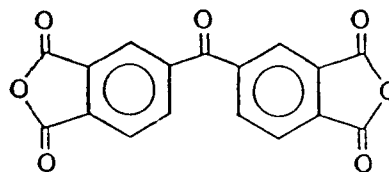
RESULTS AND DISCUSSION

Dianhydride/Diamine Structural Changes.

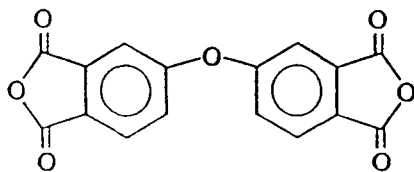
In order to determine the effect of alteration in the diamine and dianhydride portions of the polyimide films, methylenedianiline (MDA) and oxydianiline (ODA) were reacted with dianhydrides with bridging groups of oxygen (ODPA), carbonyl (BTDA), and hexafluoroisopropylidene (6F). Results from these polyimide films will be compared with those from films of pyromellitic dianhydride/oxydianiline (PMDA-ODA) and pyromellitic dianhydride/methylenedianiline (PMDA-MDA) polyimides, both of which have been shown to be quite stable upon exposure to the unfiltered output of a mercury lamp.



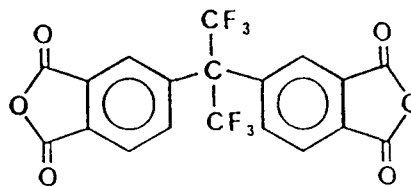
PMDA



BTDA



ODPA



6F

Previous papers focused solely on a comparison between 6F and PMDA based films (1, 2). The 6F-ODA (molecular weight at peak maxim ~26,000 compared to polystyrene) and 6F-MDA (molecular weight at peak maximum ~20,000 compared to polystyrene) films showed a rapid decrease of IR and UV absorbance which appeared to be a uniform loss

of all bands, i.e., the loss of polymer was uniform among all vibrational bands and no detectable new absorption bands appeared. Figures 1-4 show the FT-IR spectra before and after photolysis in air of thin polyimide films: PMDA-ODA, BTDA-ODA, ODDA-ODA, and 6F-ODA. All of the polyimides in Figures 1-4 were generated by an identical process (see Experimental). As shown previously, PMDA-ODA shows little change even upon extensive photolysis for 36 hours, or more. The other films all exhibit varying rates of decrease of all primary IR absorption bands. In order to provide a quantitative description of the loss of IR absorbance, the intensity of the asymmetric carbonyl stretching band with peak maximum at 1780 cm^{-1} was measured as a function of photolysis time. From the results in Figure 5, a progression in stability from PMDA-ODA (most stable) to 6F-ODA (least stable) is readily apparent. Similar results (not shown here) are obtained for photolysis of each polyimide in air when the UV absorption spectra are recorded, i.e., a uniform decrease in the UV band with shift to the blue occurs with 6F-ODA exhibiting the greatest loss. As discussed in the previous reports (1-3), these results suggest that an ablative process is operating for the photodecomposition process, at least in the presence of oxygen. This presumption is borne out by the plots of weight loss versus photolysis time for the series of films under investigation in this study: the same trend for decomposition as observed from the FT-IR absorbance loss is found for the weight loss results shown in Figure 6. In addition to the four films made in our laboratory, a commercial Kapton HTM PMDA-ODA film obtained from DuPont was also exposed and the results plotted in Figure 6 for reference. The Kapton HTM commercial sample shows enhanced stability compared to all of the films produced in our laboratory, even the

chemically identical PMDA-ODA polyimide. The enhanced stability of the commercial film may result from orientation during processing.

Similar results to those for ODA polyimides in Figures 5 and 6 are shown in Figures 7 and 8, respectively for polyimides based on the dianhydrides and MDA. The results in Figures 7 and 8 are essentially identical to those in Figures 5 and 6 indicating that, at least for the temperatures and processing conditions employed to generate the PMDA, BTDA, ODPA and 6F dianhydrides based polyimides, the ODA and MDA components cause only moderate changes in the photostability. We know, based on appropriate precedence in the literature (4-8), that as oxygen, carbonyl, and hexafluoroisopropylidene bridging groups are placed between the two imide bearing phenyl rings, as opposed to a diimide with both imides on the same ring, the delocalization of electron density found in pyromellitic dianhydride based polyimides is severely reduced. Furthermore, it has been suggested by Ishida et al. (9) and later reiterated by Frank et al. (10-12) that an aromatic chromophore on the nitrogen imide results in an sp^2 planar configuration and an imide with trigonal-planar structure. Thus, the imide moiety of the PMDA-ODA polymer would be characterized by an excited state with extensive electron delocalization and a significant contribution from a charge separated species resulting from a charge transfer process during excitation, i.e., a charge-transfer transition. Evidence for the strong charge transfer contribution to the excited state of PMDA-ODA polyimides comes from the red-shifted absorption band of PMDA-ODA (9) films which extends to well above 400 nm, the exact extent of the absorption tail being determined by both the temperature and physical treatment of the film during processing (10). Emission above 550 nm (the exact position

of the band and vibrational structure being determined by the processing temperature) has been attributed to both excitation of an intramolecular charge-transfer transition directly (for excitation by light of wavelength less than ~400nm) and by excitation of an intermolecular charge-transfer complex which has a red-extended absorption extending well above 450 nm.

What can be concluded concerning the excited charge-transfer state and consequences for the photochemistry of the aromatic polyimides based on PMDA, ODPA, and the 6F dianhydrides (BTDA is not included in this part of our study)? First, we consider the fluorescence of the PMDA-ODA, ODPA-ODA, and 6F-ODA films upon excitation at either 380 nm or 470 nm. Table I lists the emission maximum for each film as well as the excitation wavelength employed, which varies from sample to sample. The emission maxima in Table I are quoted for polyimide films cured under identical conditions (see Experimental) at 300 °C maximum: maxima will vary according to the exact curing cycle and highest cure temperatures employed. The results in Table I reflect observations for samples made according to a particular uniform cure cycle and are used solely for comparison. As pointed out by Frank et al. (10-12), and as will be seen later in this paper, the fluorescence spectra are dependent on the thermal cure temperature cycle. The absorption spectra of thin films of all three polyimides are also shown in Figure 9. Observations can be readily made concerning the emission maxima in Table I and the UV spectra in Figure 9. PMDA-ODA has a longer red-extended absorption compared to ODPA-ODA and 6F-ODA. This is also seen for the emission maxima indicating that, in accordance with observations by Frank et al. (10-12), the PMDA-ODA polyimide is

characterized by extensive delocalization in the excited state by virtue of the diimide substitution on a single phenyl ring. The ordering for PMDA-ODA and 6F-ODA emission is identical to that reported by Frank et.al (10).

We draw attention to the correlation between the emission maximum energy of the excited charge-transfer state and the stability of the polyimide films. In view of an identical trend in the magnitude of the absorption of the red-extended charge-transfer transition and position of the emission maximum with the photodecomposition rate (Figures 5 and 6), it is tempting to speculate that the photostability displayed by the PMDA-ODA film is related, at least partially, to its ability to transfer electron density in the excited state. Such an excited state distribution of electron charge might well result in enhanced stability for the PMDA-ODA polyimide in comparison to 6F and ODPA based films. However, other factors such as the stability and reactivity of intermediates produced by primary photochemical processes may also be affected by the imide structure. Of course, the 6F and ODPA based polyimides also experience some type of delocalization/charge-transfer character in the excited state, since in fact, a broad red-extended emission is also observed for each of these films.

Molecular Weight, Mode of Preparation, Processing Effects.

Having shown the dramatic difference that chemical composition imposes on the photodegradation of polyimide films, and in view of the rapid decomposition (IR, GPC changes) and ablative nature (weight loss) of the 6F-ODA samples, a more thorough

investigation of the effect of molecular weight, processing temperature and mode of polyimide formation, and sample preparation seemed necessary.

In the first section of this paper, results were presented (Figures 1-8) for photolysis of polyimides which had varying chemical structure, but were generated by an identical chemical process, i.e., a curing cycle involving casting the requisite polyamic acid followed by forced air drying at 60 °C and a subsequent heat cure for 1 hour at 100 °C, 1 hour at 200 °C, and 1.5 hours at 260 °C in air. The molecular weights of the 6F-ODA polyimides produced and evaluated by this process were about 26,000 (peak maximum in GPC compared to polystyrene standards) prior to photolysis (1). Subsequently, we have generated higher molecular weight samples (approximately 77,500) both by heat curing in an inert environment at higher temperatures and by a chemical imidization process (up to 87,500). In addition, a higher molecular weight sample was also obtained from NASA. All 6F-ODA samples show rapid degradation upon exposure to an unfiltered medium pressure mercury lamp. Specific results for the effect of cure temperature on film properties and subsequent photostability will be presented next.

In order to assess the effect of the cure temperature on the ultimate-photostability of the 6F-ODA polymers, several samples were prepared by progressive curing at higher temperatures. PMDA-ODA films were produced in an identical manner for comparison. Figures 10-13 show results for selected properties of the 6F-ODA and PMDA-ODA films cured at temperature maxima of 250 °C, 300 °C, 350 °C, and 400 °C. For 6F-ODA, there is a prominent increase in T_g (Figure 10) and the temperature required to obtain 5 percent weight loss (TGA evaluation) in air (Figure 11) as the maximum cure temperature

increases. Note that T_g 's were difficult to detect for any of the PMDA-ODA films. For both 6F-ODA and PMDA-ODA films there is a red-shift in the UV spectrum (Figure 12) accompanied by an increase in intensity and a hypsochromic shift of the fluorescence maximum (Figure 13). For both the 6F-ODA and PMDA-ODA films it should be pointed out that the extension of absorbance to longer wavelengths is not dramatic, although certainly worthy of mention. The red-shift is accompanied by an increase in structure of the emission for both 6F-ODA and PMDA-ODA films, a phenomenon proposed by Frank et al. (11) to have its origin in increased interactive aggregation in the ground state and increased coplanarization of the groups responsible for the intramolecular charge transfer transition.

The primary concern in this paper is not to demonstrate that changes occur in physical/spectroscopic properties resulting from curing at higher temperatures, but rather to ascertain their effect, if any, on the photolytic decomposition process. Adequate discussion of the consequences of curing polyimides at higher temperatures and the impact on film properties can be found elsewhere. Figures 14 and 15 show results for photolysis (unfiltered mercury lamp) of 6F-ODA and PMDA-ODA films cured with temperature maxima ranging from 250°C to 400°C corresponding to the range employed in producing films for Figures 10-13. It is apparent that there is little difference in the weight loss at a given photolysis time, despite an increase in maximum cure temperature. Apparently, the physical/spectroscopic differences produced by curing at higher temperatures do not manifest themselves in increased photostability, at least under the cure conditions employed.

Atmospheric/Radiation Source Effect.

In the results provided thus far, all of the films have been exposed to the unfiltered output of a medium pressure mercury lamp in the presence of oxygen. Thus, the sample films have been subjected to primary mercury lines from the deep UV (below 300nm) to the near UV(300-400nm) and visible (>400 nm). The potential for photooxidation is quite high, especially since film surfaces are in contact with both oxygen and high photon fluxes, a combination well-suited to oxidative ablation. Results in this section are reported for exposure to three additional sources: electron-beam irradiation in vacuum, Pyrex filtered (>300nm) irradiation of a medium pressure mercury lamp in air, and unfiltered medium pressure mercury lamp in a nitrogen atmosphere. Combined with the results already reported for irradiation by an unfiltered medium pressure mercury lamp in air, a clearer picture of the photodegradation process of polyimide films begins to emerge.

Figure 16 shows results for the change in molecular weight (peak maximum-referenced to polystyrene) of 6F-ODA polyimide films as a function of photolysis time with both the unfiltered (curve a) and filtered (curve b) output of a mercury lamp. The 6F-ODA sample with a starting molecular weight of 77,500 rapidly decomposes in both cases, although the decomposition is much faster for exposure to the unfiltered light. This is certainly reasonable since several quite intense mercury lines below 300 nm are rejected by the Pyrex filter. What is probably the most surprising result is the lack of significant change in IR spectral bands for photolysis of 6F-ODA films with unfiltered and filtered light.

Minor IR changes are noted for 6F-ODA films after photolysis with the Pyrex filtered lamp whereas, as shown already, the molecular weight loss for photolysis with the unfiltered lamp is accompanied by significant losses in all IR bands as well as film mass. Thus, even though the molecular weights for 6F-ODA polyimide films may be similar after photolysis with either an unfiltered or filtered mercury lamp, there is much less change in the IR band intensities for the sample photolyzed with the Pyrex filtered mercury lamp. Of course longer times of photolysis are required to reach a given molecular weight when the lamp is filtered with Pyrex. Thus, while the molecular weight change is induced by light both above as well as below 300 nm, the subsequent photoablative process requires light below 300 nm to induce an efficient uniform decrease in the IR. The question of whether oxygen must be present in order for chain cleavage to be effective remains to be answered.

Additional information concerning the effect of oxygen on chain cleavage is obtained from photolysis with the unfiltered mercury lamp of the film in a nitrogen atmosphere. As seen in Figure 17, there is no decrease in any of the IR bands after photolysis for 96 hours in nitrogen with the unfiltered mercury lamp. Likewise there is almost no decrease in the polyimide molecular weight upon photolysis for 96 hours. (Of course, photolysis with the unfiltered output in nitrogen also results in no perceptible decomposition). These results are particularly significant since they indicate that oxygen is also necessary for the chain-scission process leading to the molecular weight decrease as well as the subsequent photoablative process with the medium pressure mercury lamp.

In summarizing the results for photolysis in air with the filtered mercury lamp and in nitrogen with the unfiltered lamp, several features of the photodegradation process emerge. First, the photoinduced chain-scission occurs by exposure to light of wavelength greater than 300 nm providing that oxygen is present during photolysis. Second, the subsequent photoinduced oxidative degradation process requires light of wavelength less than 300 nm for rapid decomposition following the chain-cleavage process to occur. This suggests that the products of the initial photoinduced chain cleavage process which are responsible for completing the relatively rapid photooxidative ablation process primarily absorb light of wavelength less than 300 nm. Since primary cleavage is theoretically possible at a number of sites for the 6F-ODA polymer, and defining the exact mechanism is quite complex, the discussion of the sequence of photooxidative events responsible for the photooxidative degradation process will be published under separate cover.

One final source for irradiation of 6F-ODA, an electron beam, was also employed in an attempt to induce decomposition of a 6F-ODA film. A 6F-ODA thin film was subjected to electron beam irradiation and analyzed for compositional changes in the film by transmission IR and evolution of gaseous photoproducts in an IR gas cell. The 6F-ODA, produced by a maximum cure temperatures of 300 °C, was spin cast on a NaCl window from a THF solution to give a film of 0.8 microns. Upon exposure in an argon atmosphere to 429 MRad radiation from the electron beam, no change could be detected in the transmission IR spectrum (not shown), and no gaseous products could be detected upon analysis of the atmosphere above the films. As a result of these analyses, the 6F-ODA films in argon are termed "radiation dead" to electron beam irradiation, at least up

to doses of over 400 MRads (we have even exposed samples to 520 MRad with no apparent decomposition).

CONCLUSION

In summarizing the results of the present investigation of the photolysis of polyimide films, we have evaluated the effect of chemical structure, processing temperature, and irradiation source/atmosphere. The most dramatic effect of chemical structure occurs with the incorporation of dianhydrides connected by relatively flexible, as opposed to the single phenyl ring of pyromellitic dianhydride, bridging or hinge moieties such as carbonyl, oxygen, or hexafluoroisopropylidene. The hexafluoroisopropylidene based dianhydride (6F) results in generation of an extremely photochemically reactive polyimide compared to pyromellitic dianhydride (PMDA) based polyimides. Even though processing conditions and temperature can alter the glass transition, thermal decomposition temperature, absorption and emission spectra, and related physical and spectroscopic properties of polyimide films based on reaction of 6F and PMDA with oxydianiline (ODA), there is no perceptible difference in the propensity for photolytic decomposition. However, the atmosphere in which the polyimide film is irradiated and the spectral characteristics of the photolysis source can dramatically alter the degradation process. When photolysis of 6F-ODA films is conducted in the presence of oxygen using light with wavelength greater than 300 nm (Pyrex filtered medium pressure mercury lamp), chain-scission is rapid in comparison to the subsequent photooxidative ablation process. Photolysis with the unfiltered mercury lamp, however, results in both chain-scission and subsequent rapid photooxidative decomposition. Thus,

the complete photooxidation process requires photolysis with light below 300 nm to produce both chain scission and photooxidative ablation efficiently. Furthermore, neither appreciable chain scission (as detected by GPC) nor decomposition of any functional groups (as analyzed by IR) occurs when 6F-ODA films are exposed to the unfiltered output of the mercury lamp for extensive time periods in nitrogen. This indicates that both main chain scission as well as the process leading to efficient and complete decomposition of the 6F-ODA polyimide require the presence of oxygen. The mechanism for the photooxidative ablation process, which involves formation of anhydrides and subsequent photolytic decomposition of primary photoproducts, will be published in other manuscripts. Future work will deal with the effect of using different diamines on the photooxidative decomposition of polyimide films.

ACKNOWLEDGEMENT

We acknowledge the financial support of the Office of Naval Research. The help of Jake Pacansky of IBM in performing the electron beam irradiation is also acknowledged.

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Table I			
Polymer	Max Cure Temp (°C)	$\lambda_{\text{excitation}}$ (nm)	$\lambda^{\text{max}}_{\text{emission}}$ (nm)
6F-ODA	300	380	508
ODPA-ODA	300	380	505
PMDA-ODA	300	450	566

FIGURE CAPTIONS

- Figure 1. IR spectral change on photolysis of PMDA-ODA film in air using an unfiltered medium pressure mercury lamp. (a) 0 h; (b) 36 h. Reprinted from *J. Appl. Polym. Sci.*, 43, (1), 1 (1991).
- Figure 2. IR spectral change on photolysis of 6F-ODA film using an unfiltered medium pressure mercury lamp. (a) 0 h; (b) 20 h. Reprinted from *J. Appl. Polym. Sci.*, 43, (1), 1 (1991).
- Figure 3. IR spectral change on photolysis of BTDA-ODA film using an unfiltered medium pressure mercury lamp. (a) 0 h; (b) 36 h.
- Figure 4. IR spectral change on photolysis of ODPA-ODA film using an unfiltered medium pressure mercury lamp. (a) 0 h; (b) 36 h.
- Figure 5. Plot of relative intensity of asymmetric carbonyl stretch at 1780 cm^{-1} versus time for photolysis of ODA based polyimide films with unfiltered medium pressure mercury lamp in air.
- Figure 6. Plot of weight loss versus time for photolysis of MDA based polyimide films with unfiltered medium pressure mercury lamp in air. (Film is 14.5 cm^2).
- Figure 7. Plot of relative intensity of asymmetric carbonyl stretch of 1780 cm^{-1} versus time for photolysis of MDA based polyimide films with unfiltered medium pressure mercury lamp in air.
- Figure 8. Plot of weight loss versus time for photolysis of ODA based polyimide films with unfiltered medium pressure mercury lamp in air.

- Figure 9. Absorption spectra of thin ODA based polyimide films cured at 300 °C on quartz slides.
- Figure 10. Glass transitions of 6F-ODA films as a function of the maximum cure temperature.
- Figure 11. Temperature for 5% weight loss in nitrogen as function of the maximum cure temperature for 6F-ODA and PMDA-ODA films.
- Figure 12. UV spectra as a function of maximum cure temperature for (a) 6F-ODA (b) PMDA-ODA films.
- Figure 13. Fluorescence spectra of (a) 6F-ODA films, and (b) PMDA-ODA films cured at several maximum temperatures and excited at 370 nm.
- Figure 14. Weight loss as a function of photolysis time for 6F-ODA films cured at maximum temperatures ranging from 250 °C to 400 °C. (Film area is 4.0 cm²)
- Figure 15. Weight loss as a function of photolysis time for PMDA-ODA films cured at maximum temperatures ranging from 250 °C to 400 °C. (Film area is 4.0 cm²)
- Figure 16. Peak maximum molecular weight (compared to polystyrene standards) as a function of time for photolysis of 6F-ODA films with (a) an unfiltered medium pressure mercury lamp in air (b) a filtered (Pyrex) medium pressure mercury lamp in air.
- Figure 17. IR spectral change on photolysis of 6F-ODA film in nitrogen using an unfiltered medium pressure mercury lamp for (a) 0 h; (b) 96 h.

Fig. 1

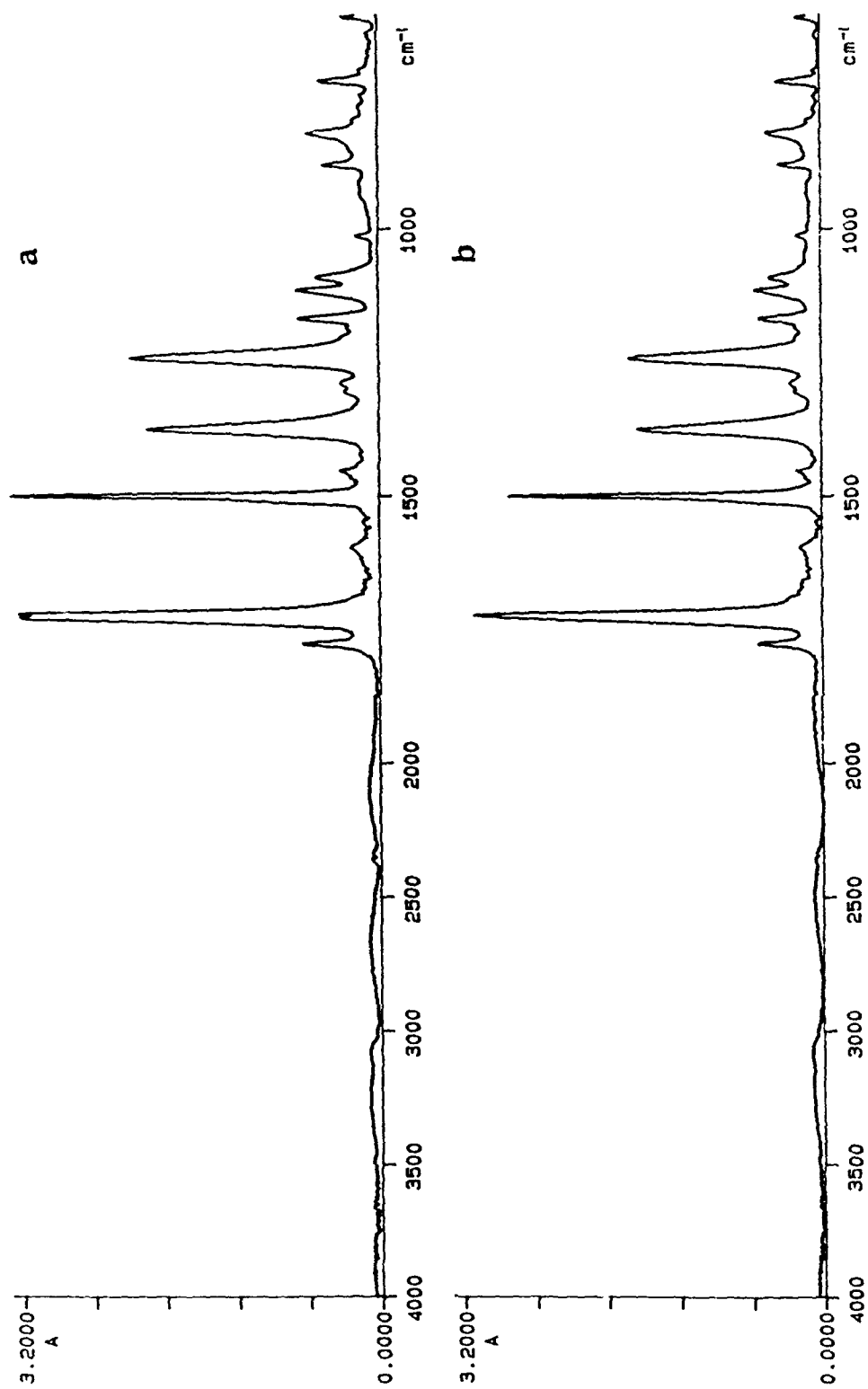


Fig. 2

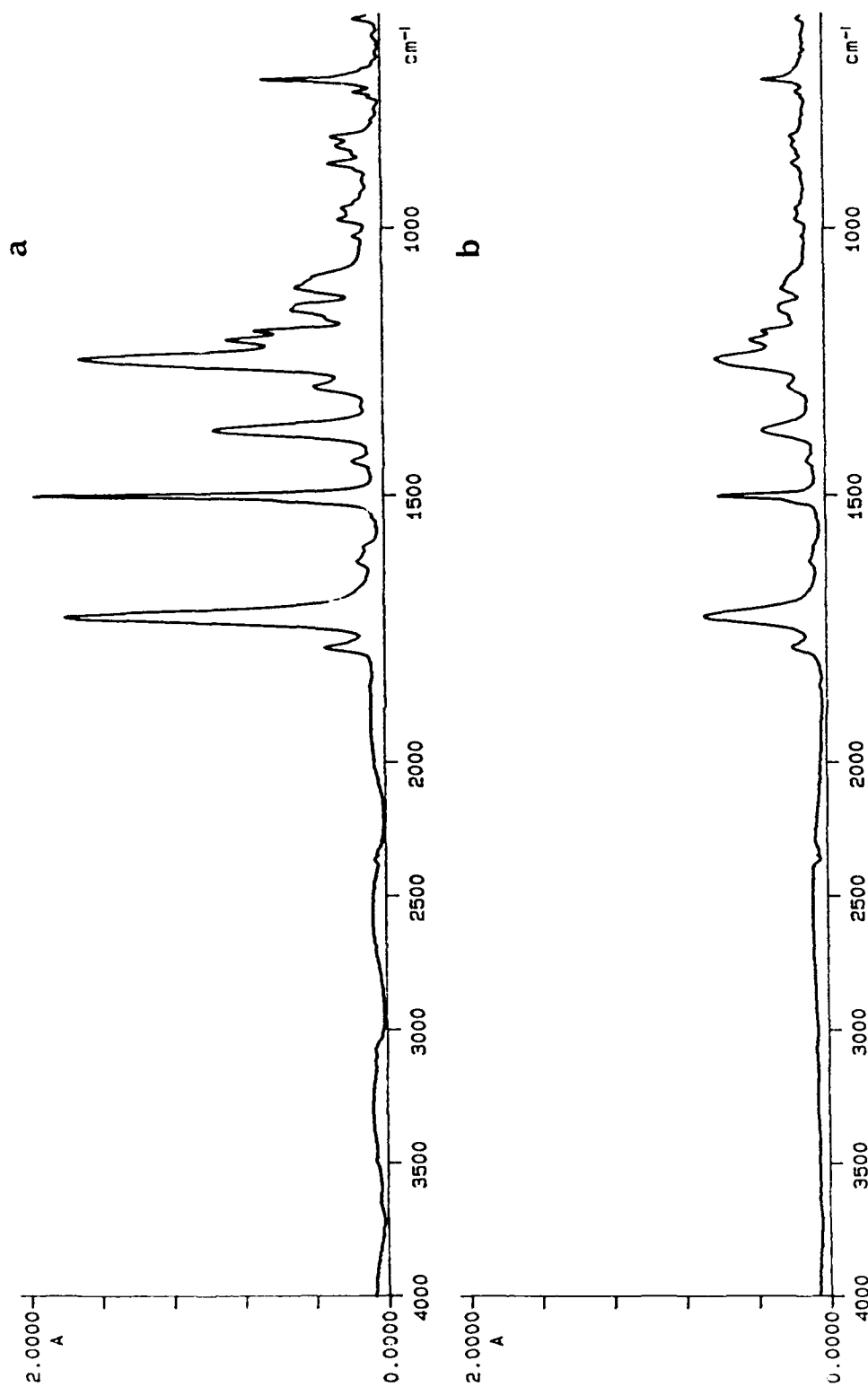


Fig. 3

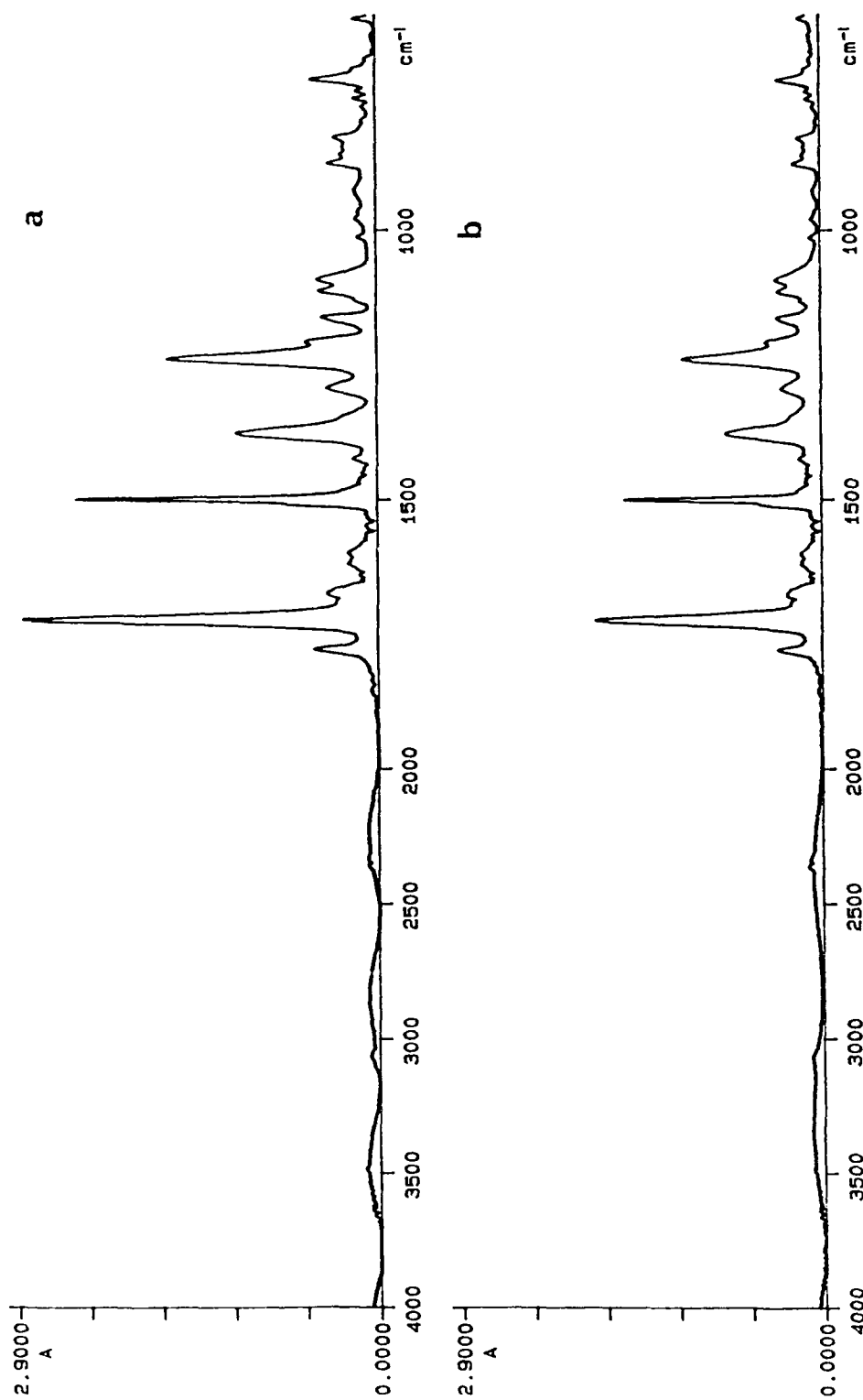


Fig. 4.

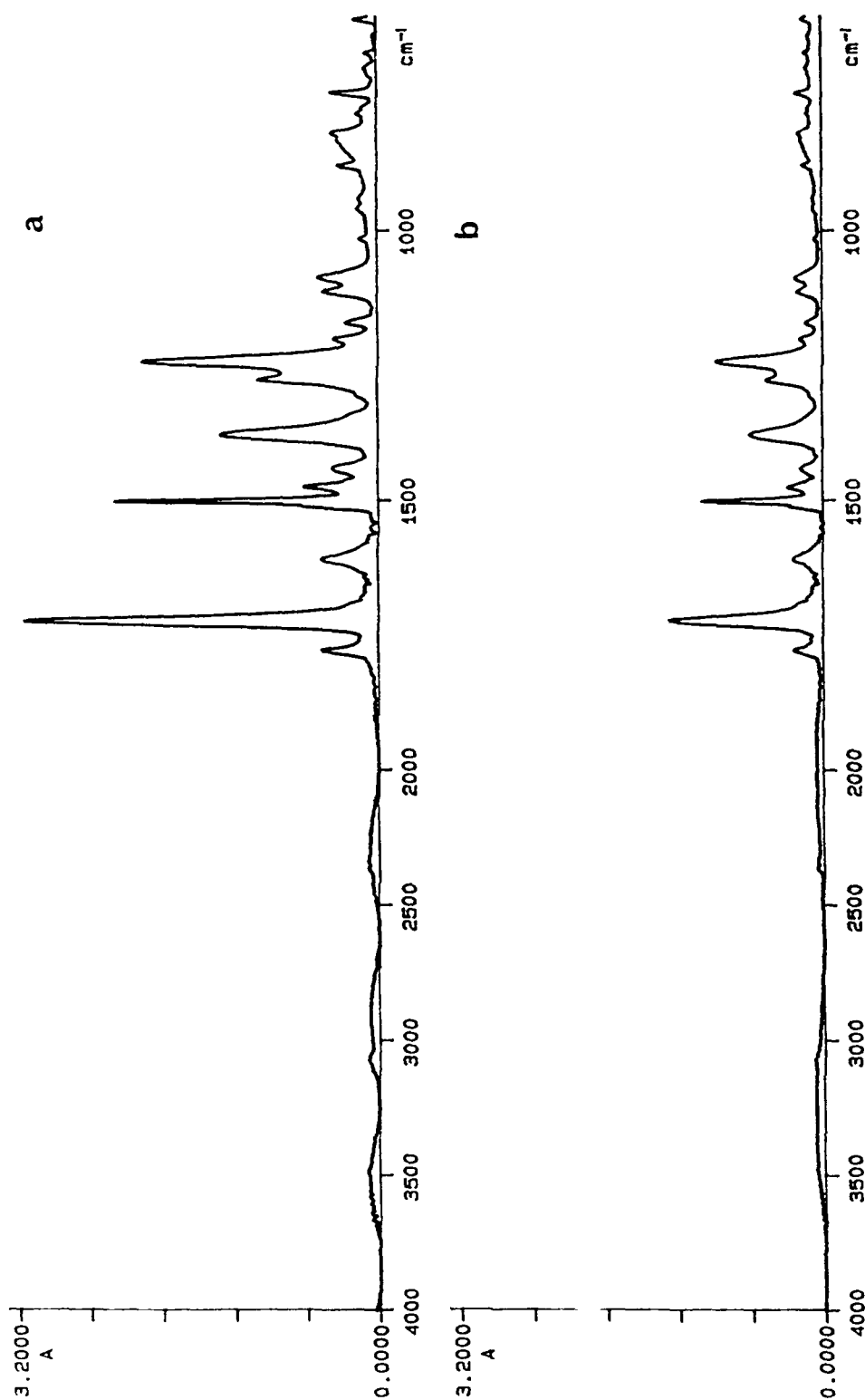
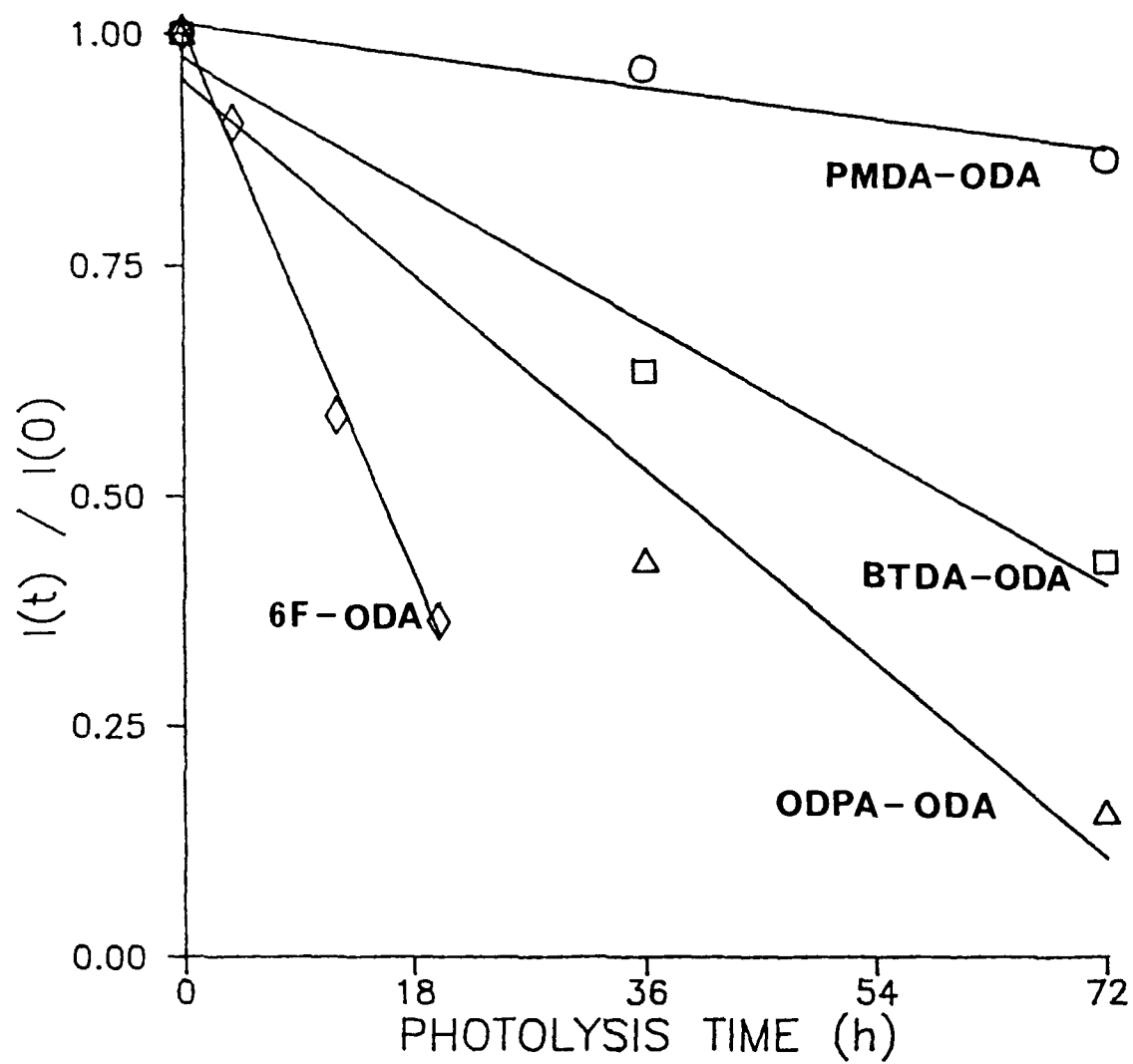


Fig. 5



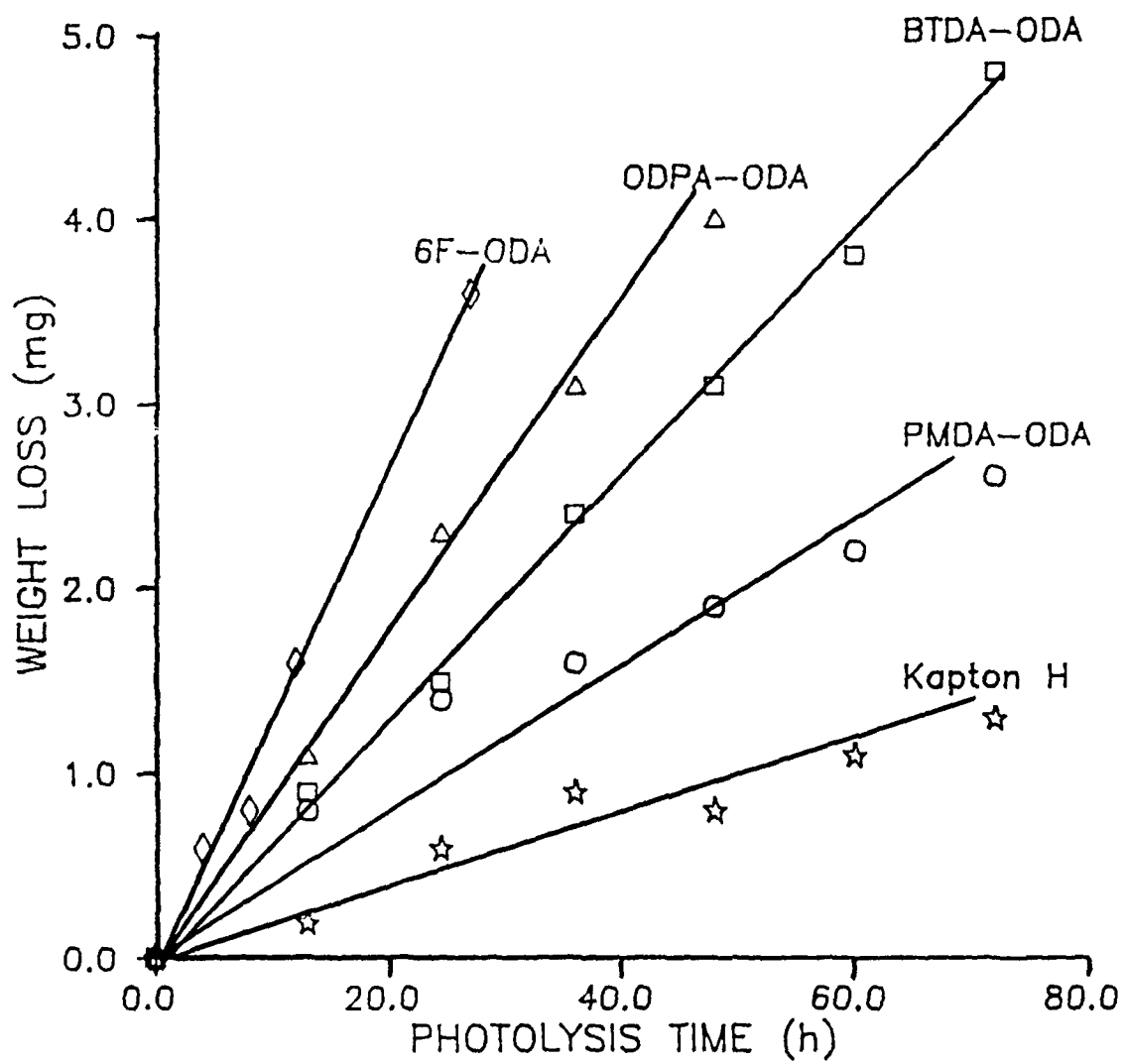


Fig. 7

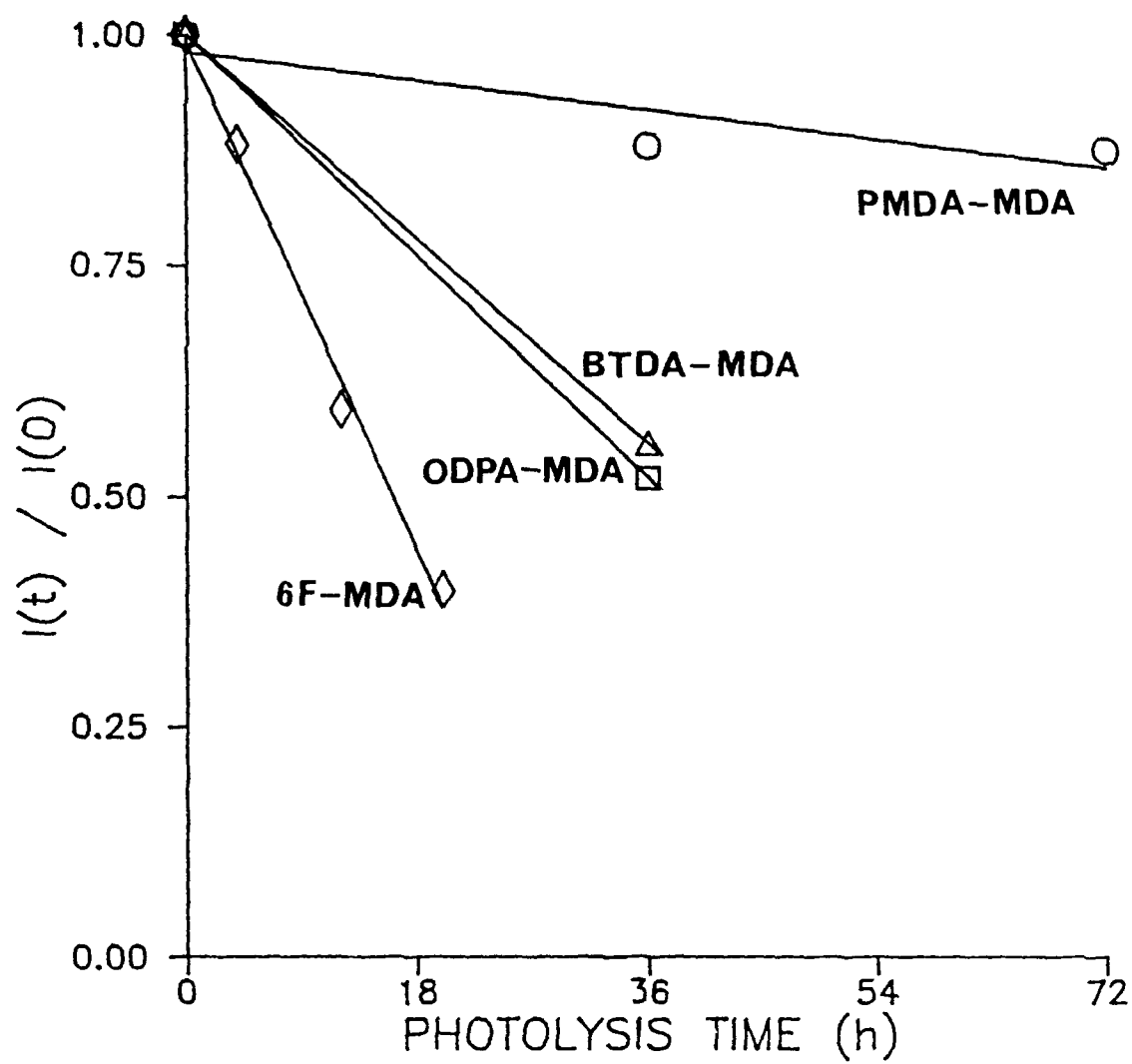


Fig. 8

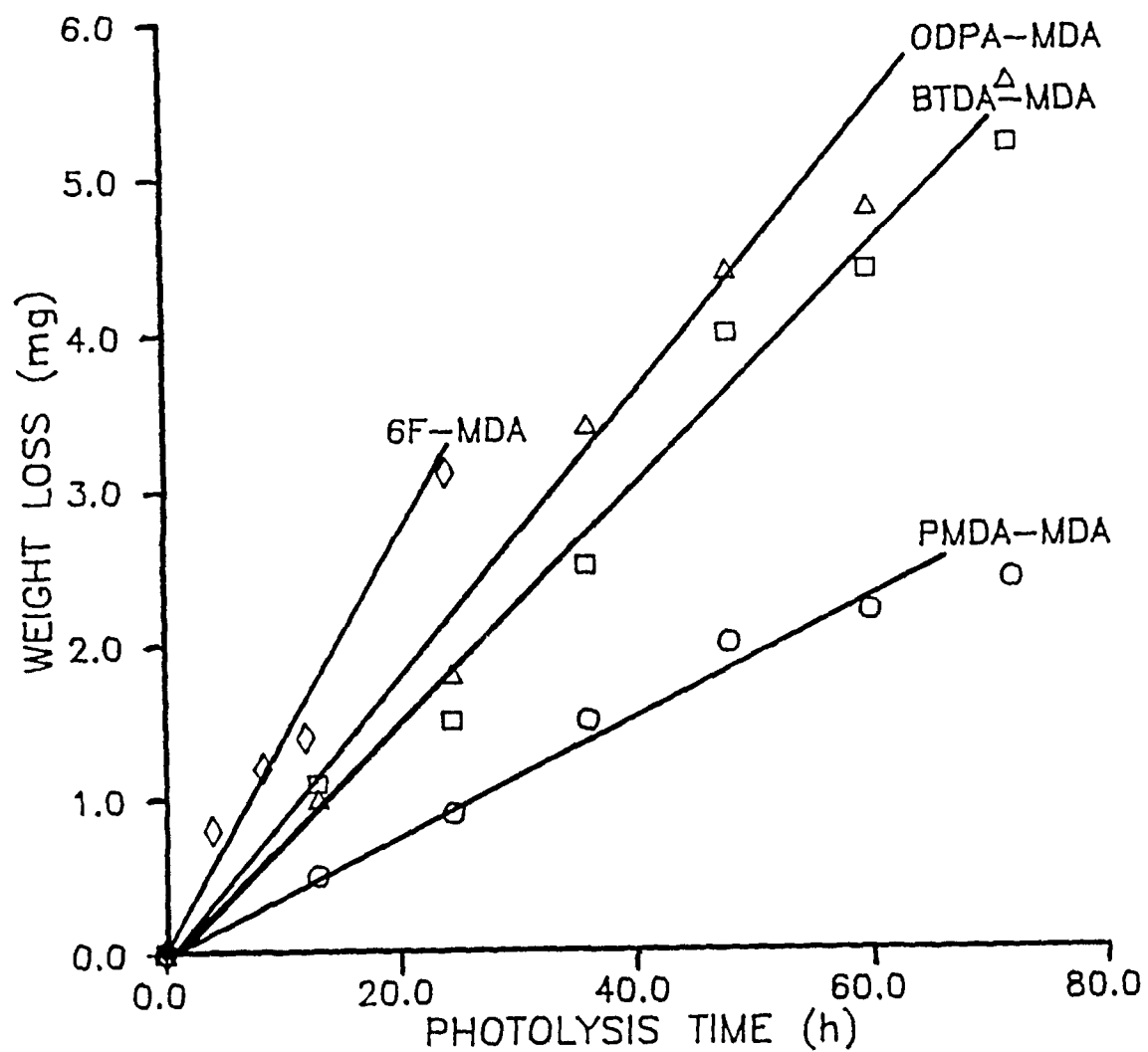
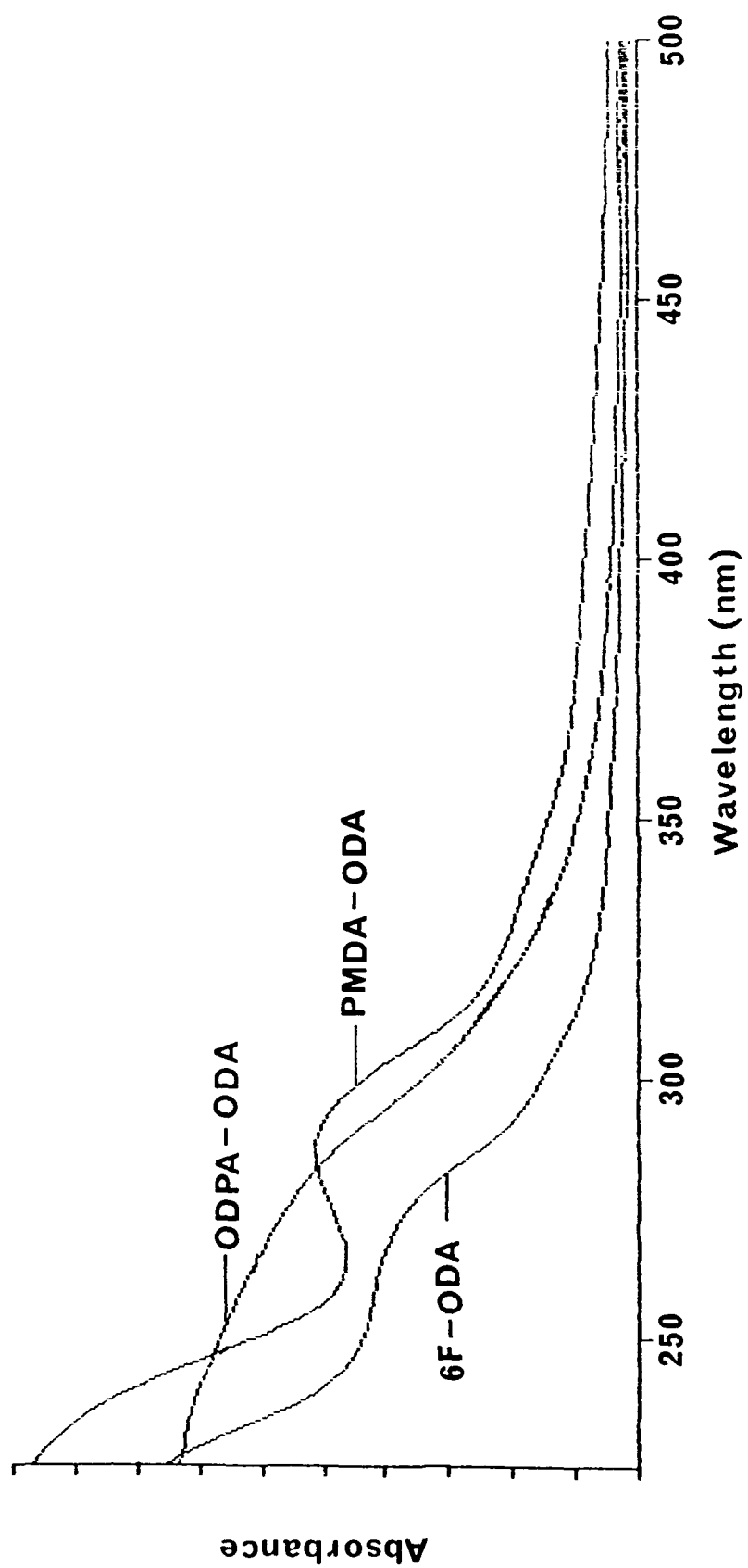
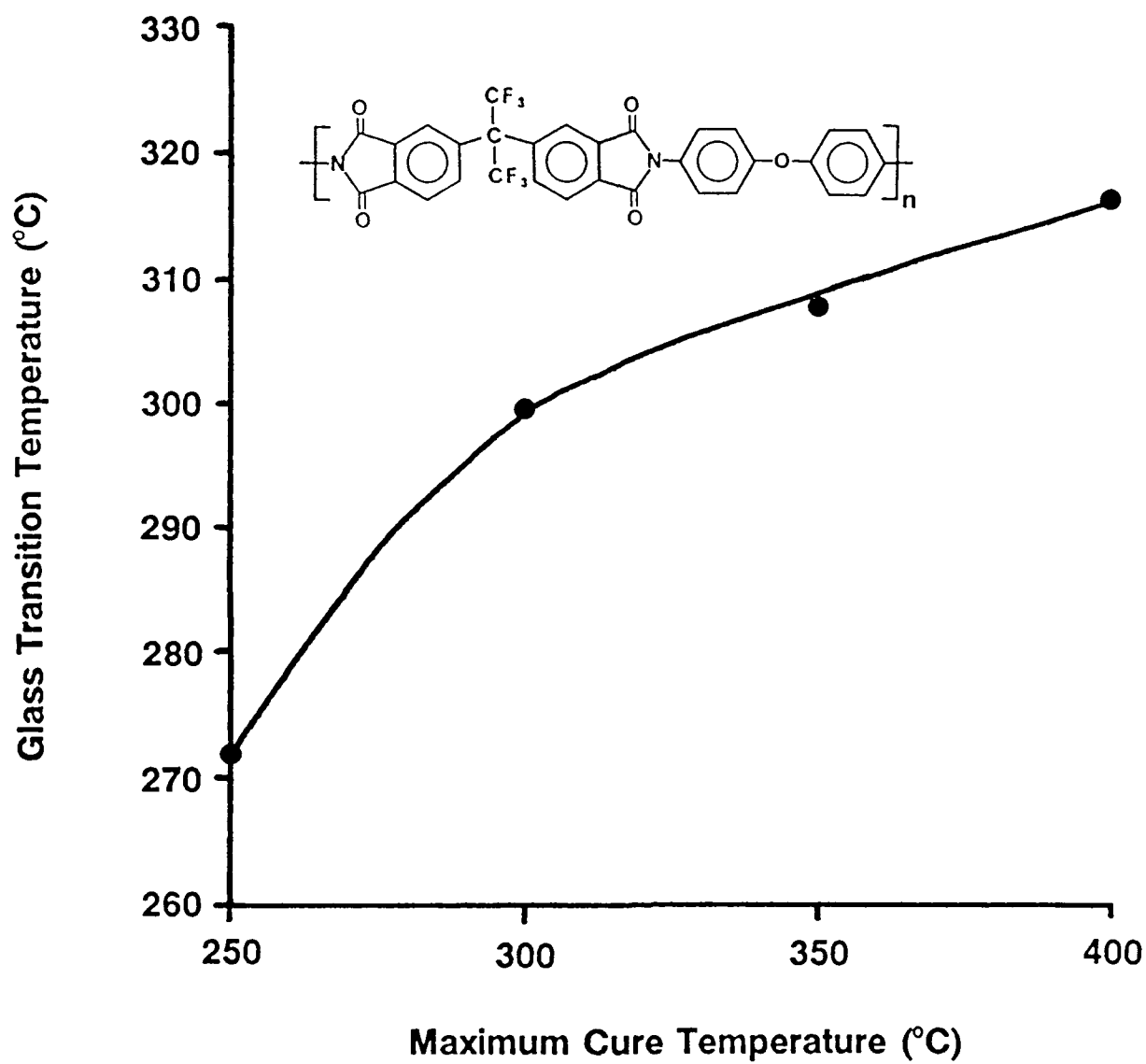


Fig. 1





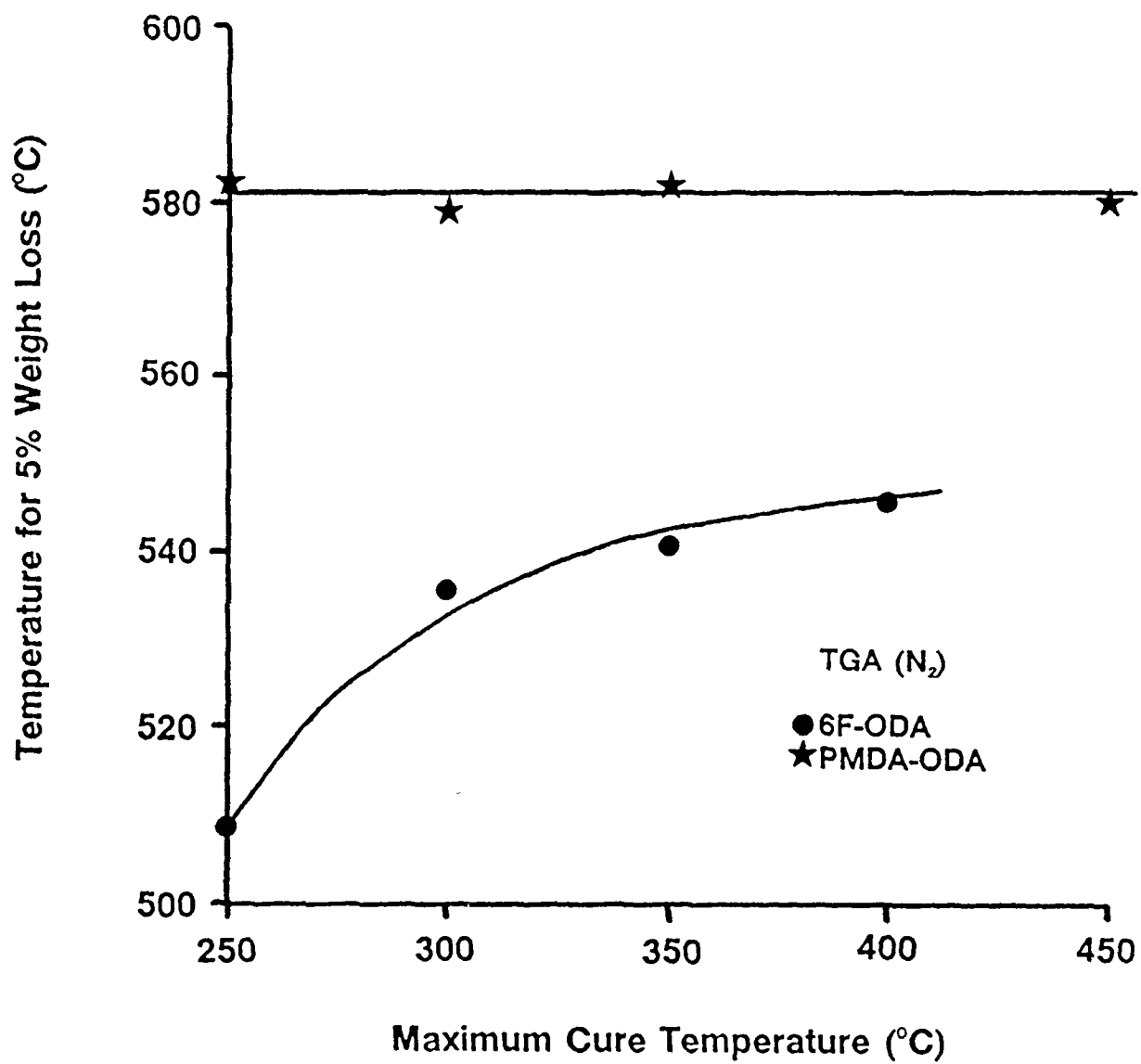
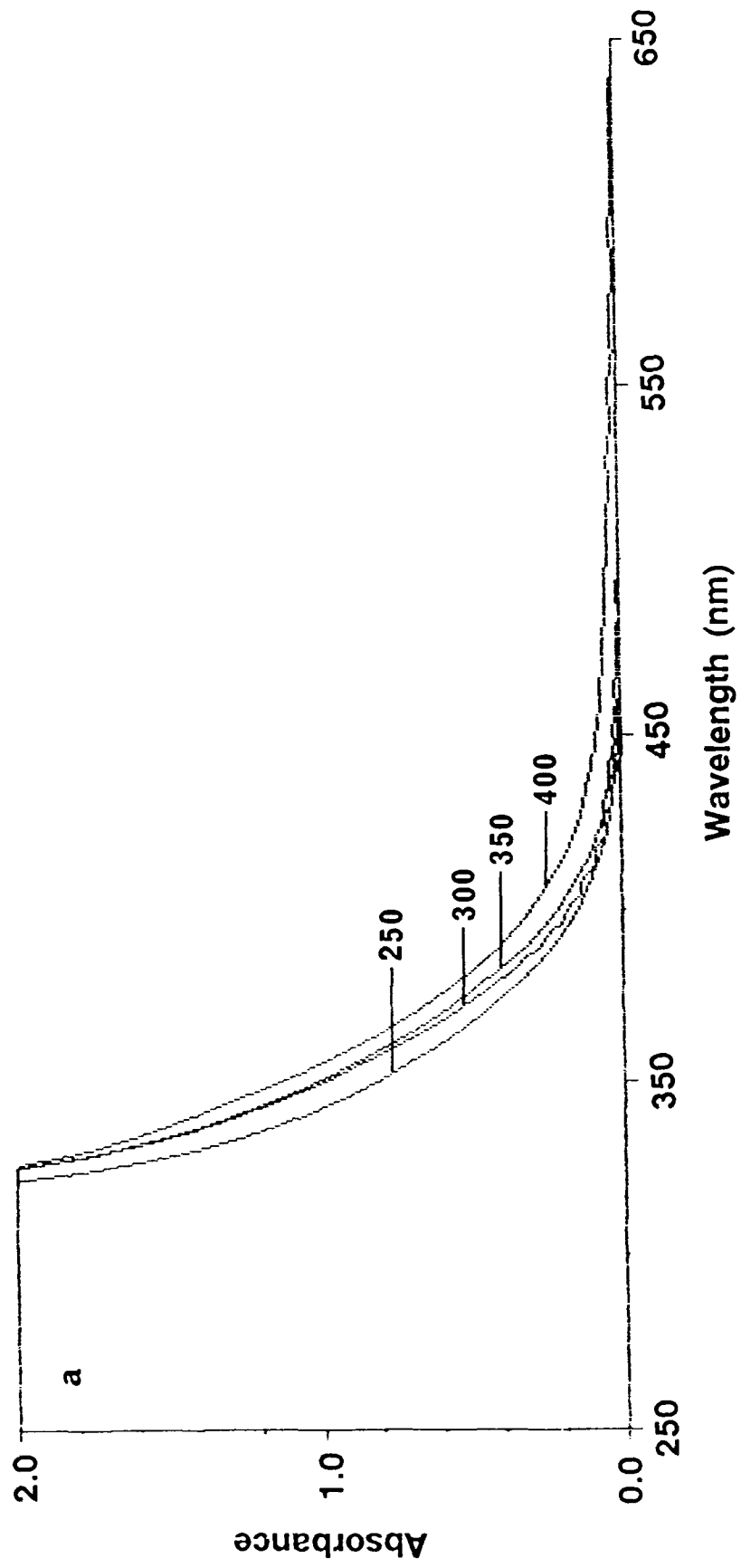
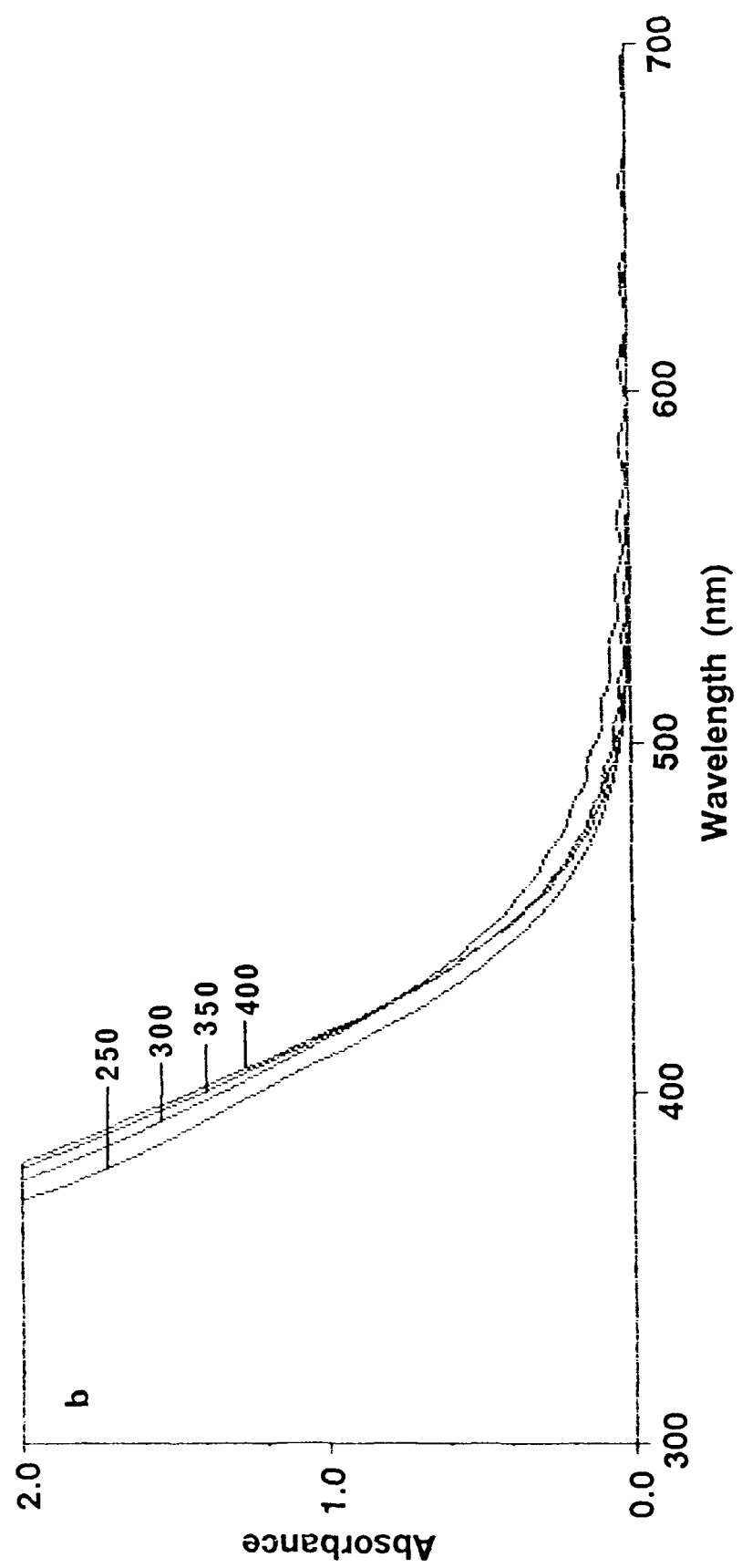


Fig. 2a





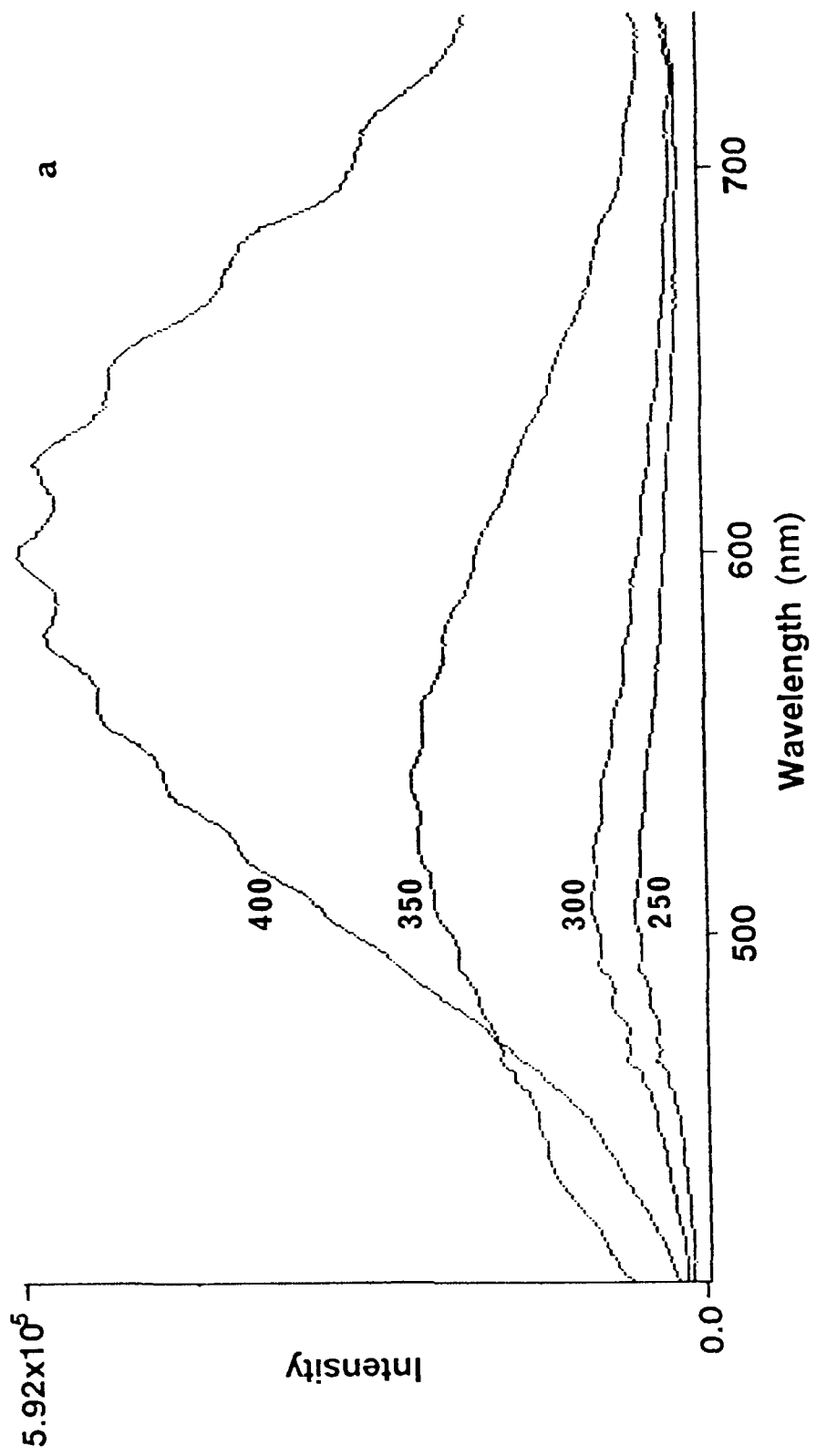


Fig. 13a

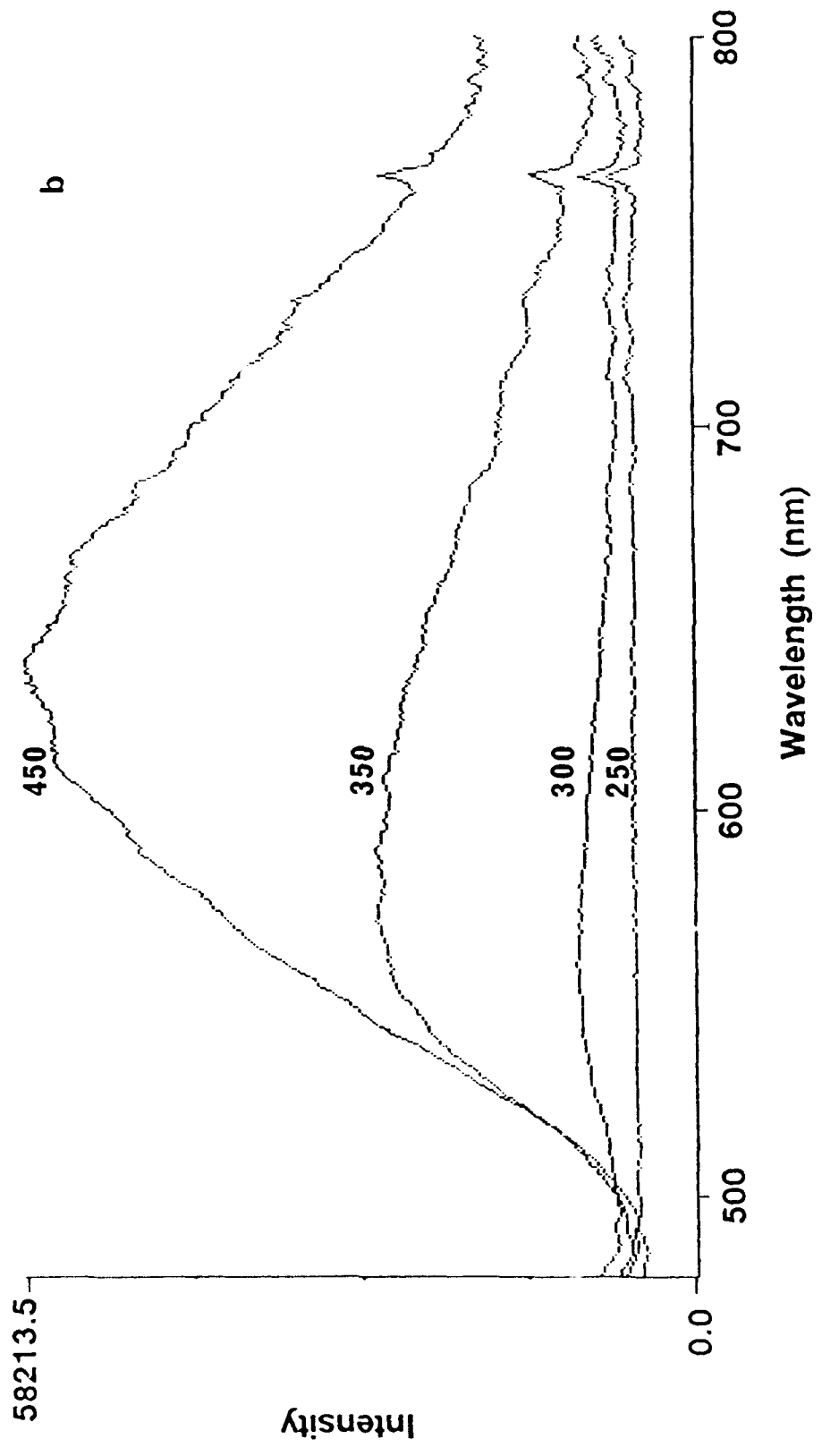


Fig. 14

